

Observing transient chemical changes by ultrafast x-ray absorption spectroscopy

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INTRODUCTION

With the advent of femtosecond (fs) time resolution in spectroscopic experiments, it is possible to study the evolution of nuclear motions in chemical and photochemical reactions. In general, the reaction is clocked by an initial fs laser pulse (which establishes the zero of time) and the dynamics are probed by conventional spectroscopy. Replacing the probe laser with an X-ray pulse to perform X-ray absorption (XAS) holds the promise of directly observing the change of electronic structure (via x-ray near-edge absorption: XANES) and of the atomic motions (via x-ray absorption fine structure: XAFS). So far time-resolved XAS has been limited to the ms-ns time domain. Here we report the detection of transient chemical changes in the picosecond time domain, upon ultrashort laser pulse excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ in a water solution. We are able to detect the change of oxidation state of the Ru atom with the zero of time unambiguously established. These results provide us with a means to prospect future time-resolved XAS experiments for the direct observation of the underlying nuclear dynamics in solids, liquids and dense gases by which chemical and biochemical reactions occur.

RESULTS

The experiments were carried out at bend magnet beamline 5.3.1 of the Advanced Light Source (ALS). The storage ring is filled with several 2 ns-spaced bunches generating a ca. 550 ns long "superbunch", followed by a ca. 100 ns dark section, in which one single electron bunch (called the "camshaft pulse" at the ALS, or the "hybrid" pulse at other synchrotrons) is placed. This filling pattern permits us to record the intensity of this single x-ray pulse with a suitably fast (and sensitive) avalanche photodiode (APD) detector. The amplified femtosecond laser is synchronized to this single pulse, so that a single camshaft pulse at a fixed time delay follows every laser pulse at 1 kHz repetition rate.

The tris-(2,2'-bipyridine) ruthenium (II) complex has served as a paradigm for optically prepared Franck-Condon excited states of transition metal complexes. Light absorption by $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ results in the formation of a Franck-Condon metal-to-ligand charge transfer singlet $^1(\text{MLCT})$ excited state, which undergoes subpicosecond intersystem crossing to a long-lived triplet $^3(\text{MLCT})$ excited state¹. This reaction involves a change of oxidation state of the Ru central atom and a change of structure of the complex (in order to transform into the C_2 symmetry), both of which can be probed by X-ray absorption using XANES and EXAFS in the ruthenium L-edge region. Here we concentrate on XANES in which very sharp peaks are observed.

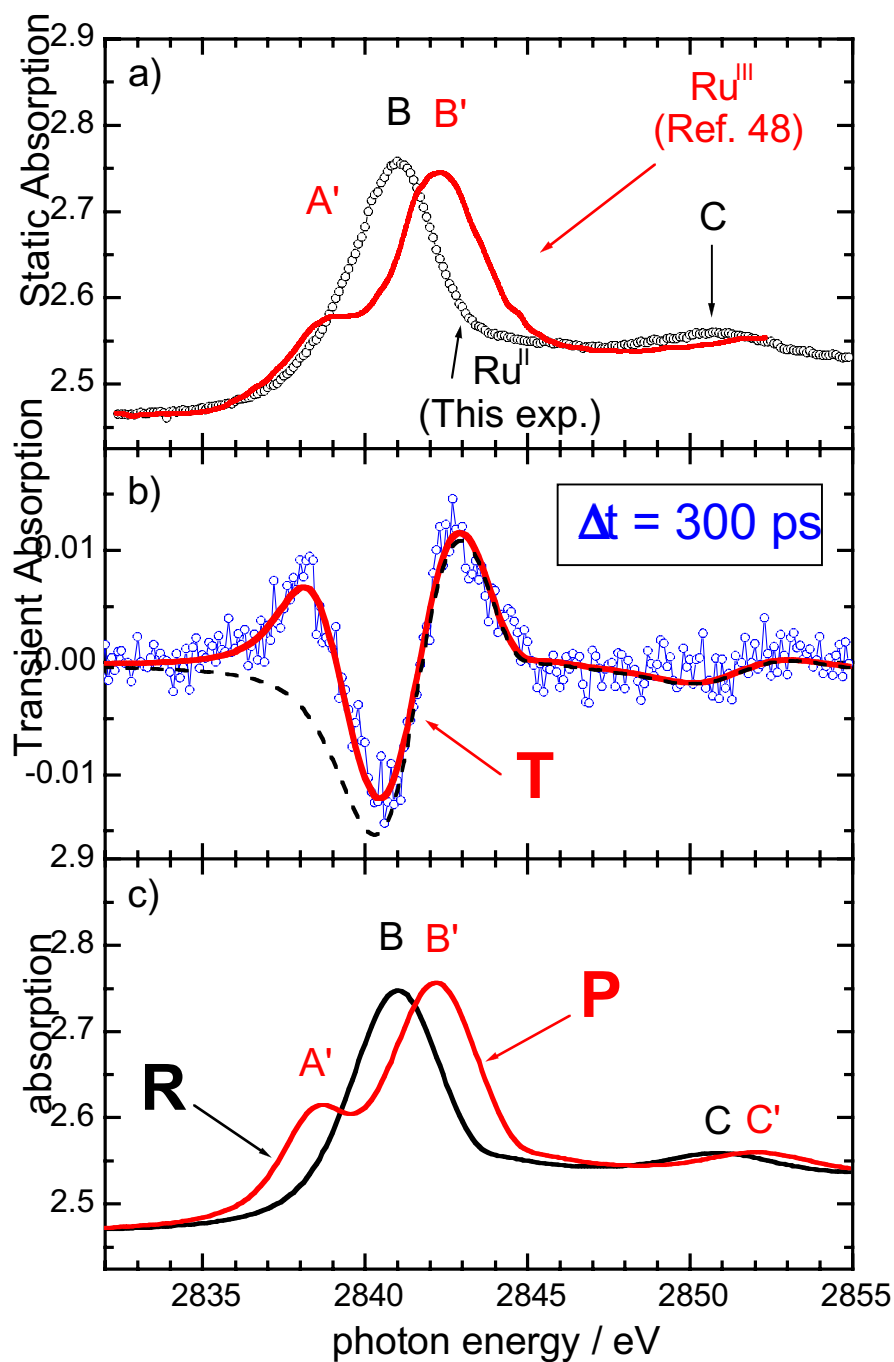


Figure 1. (a) Static X-Ray absorption spectra at the Ru L_3 edge of aqueous $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (open circles, this experiment), and of $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_2$. (b) Transient absorption spectrum after 300 ps of photoexcited $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (open circles) together with a fit (solid curve T), from which the product state absorption spectrum in c) was generated. (c) Reactant state absorption spectrum ((R) fitted from the experimental data in a) and intermediate compound absorption spectrum P constructed from the reactant state R and the transient absorption spectrum T. The labeled features A', B', C', and B, C denote the allowed transitions of Ru^{III} and Ru^{II} , respectively.

The different oxidation states of Ru^{II} and Ru^{III} complexes exhibit pronounced differences in their XANES. This is shown in Fig. 1a for aqueous $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$, measured around the Ru L_3 edge. A pre edge absorption feature at 2841.0 eV (denoted B in Fig. 1a) characterizes the bivalent compounds due to the $2p_{3/2} \rightarrow 4d_{3/2}$ (e_g) transition, next to the weaker $2p_{3/2} \rightarrow 5s_{1/2}$ transition around 2851 eV (feature C). Removal of the weakest bound

electron from the fully occupied $4d_{3/2}$ (t_{2g}) level generates a trivalent ruthenium compound, and this opens up an additional absorption due to the allowed $2p_{3/2} \rightarrow 4d_{5/2}$ (t_{2g}) (feature A') next to an overall oxidation state induced energetic shift. Thus we observe a doublet structure A' and B' in the trivalent L_3 XANES together with a ca. 1 eV energetic $B \rightarrow B'$ and $C \rightarrow C'$ shift (Fig. 1a). Therefore, formation of $^3(\text{MLCT})$ transient should lead to the appearance of this doublet structure in the L_3 XANES as a consequence of the change of oxidation state of the Ru central atom. Fig. 1b shows the transient absorption spectrum recorded 300 ps after laser excitation. This transient contains all the electronic changes between the reactant state absorption and the product state absorption spectrum. Thus we can directly deduce the XANES of the unknown reaction intermediate from this transient signal. The fitted XAS is shown in Fig. 1c as the curve R. To date, no XAS exists for the transient species $[\text{Ru}^{\text{III}}(\text{bpy}^-)(\text{bpy})_2]^{2+}$ (curve P in Fig. 1c), but we can compare our spectrum with the static XAS of the isoelectronic species $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ shown in Fig. 1a. Indeed, the spectra are very similar with identical A'-B' splitting and A'/B' relative intensities, which indicates a nearly identical electronic configuration of the complexed central Ru atom.

REFERENCES

1 *Differences between L_3 and L_2 x-ray absorption spectra of transition metal compounds*
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This work was funded by the Swiss National Science Foundation via contracts no. 2000-059146.99 and 620-66145.01, by the Swiss Light Source (SLS), and by the Advanced Light Source (ALS).

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